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(54) Title: METHOD FOR DECONTAMINATION

(57) Abstract

Decontamination by removal of a surface layer, generated or deposited on a material surface, wherein a decontamination agent is applied to said surface layer and a microwave field is applied to act on said deposited surface layer and the decontamination agent applied thereto to improve the penetration of the decontamination agent, the disintegration and at least partial dissolution as well as the removal of the surface layer, and to shorten the treatment time with a low addition of decontamination agent.

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Method for decontamination

TECHNICAL FIELD

The invention relates to a method for decontamination in which a surface layer deposited or generated on a surface is completely or partially removed.

BACKGROUND ART

On materials included in a nuclear power plant, surface layers comprising, for example, corrosion products containing radioactive nuclides are deposited or generated during operation.

The above-mentioned deposited surface layers must be regularly removed, among other things to provide low dose rates, during inspection and maintenance, to reduce the exposure of personnel concerned to radioactive radiation, whereby the importance of decontamination increases. Allowed or recommended maximum levels have been established by authorities and international bodies, such as, for example, by ALARA.

Decontamination means that the above-mentioned surface deposits, which usually contain radioactive nuclides, are removed and taken care of, which can be done with chemical, mechanical, and electrochemical methods. With chemical methods, surfaces are reached which are difficult to reach with other methods. However, in the day-to-day work, it is preferred to avoid handling hazardous chemicals, and, therefore, mechanical methods such as high-pressure washing and blasting as well as electrochemical methods such as the decontamination process ELDECON, developed by ABB Atom AB, are used to a considerable extent. Also methods such as ultrasonic washing and washing with solvents as well as carbon monoxide blasting are used to a limited extent.

In chemical decontamination, low-concentration processes based on organic acids or containing slightly oxidizing reagents, LOMI (Low Oxidation state Metal Ion), are preferably used today. The non-regenerative LOMI method has been used exclusively in decontamination of reactor recirculation and RWCU (Reactor Water Clean Up) systems.

Processes based on organic acids which are suitable for boiling water reactors (BWRs) are, for example;

- CITROX, developed by PNS, which is based on citric and oxalic acid, comprising regeneration and ion exchange,

- CAN-DEREM, developed by LN Technologies, which is an oxalic-acid free version of the CAN-DECON process, and

- CORD, developed by Siemens/KWU, which comprises oxidation with permanganic acid followed by a treatment with a diluted organic acid.

Methods which have still only been tested for treatment of pressurized-water reactors (PWRs) comprise the VS (Very Soft) process developed by Asea Brown Boveri AB, the Conap process developed by Westinghouse, the POD process and the DCD process developed by CEGB.

The VS process comprises an oxidation with a weak permanganic and chromic acid followed by a removal of the softened oxide layers by a reduction or a non-chemical method. The POD process comprises a treatment with nitric acid and permanganate followed by a treatment with citric acid and oxalic acid whereas the DCD process is based on citric acid and oxalic acid.

In addition, there exists a decontamination process based on ozone, ODP (Ozone Decontamination Process), developed by ABB

Atom AB and Studsvik, which is a one-step process at room temperature.

Mechanical processes comprise blasting, brushing, high-pressure washing etc. These methods are generally less versatile and are used substantially on external surfaces or surfaces which in some other way can be made accessible from outside. In certain situations these mechanical methods may increase the local corrosion since they give rise to mechanical stresses in the treated material. In addition, the treatment results in a coarse surface with a considerable propensity for recontamination.

Electrochemical decontamination is based on anodic dissolution of the oxide layers. The object being treated is arranged as an anode in an electrolytic cell. The general advantages of electrochemical decontamination are the high decontamination factors, the short treatment times, the low volumes of waste, and the smooth surfaces resulting from the treatment which results in reduced propensity for recontamination.

The ELDECON process is characterized by alternately anodic and cathodic treatment in a neutral, non-aggressive solution. The electrolyte is not consumed during the process. Furthermore, the volume of waste is small and compatible with all common processes for solidification of waste.

Although decontamination has increasingly become routine within the nuclear power industry, certain aspects still need to be considered. Earlier, corrosion itself was the main problem, especially for decontamination of the entire system. However, with increasing experience from decontamination, other issues come into focus, such as influence on and protection of components included in the system, such as, for example, gaskets, especially in pumps, risks of recontamina-

tion, and treatment of the resulting waste.

In chemical decontamination of the whole system, it is important that the treatment agent reaches out in the whole system. The agent can be added all at a time according to a so-called fill-and-drain process, or be added gradually according to the so-called feed-and-bleed process. The latter has the advantage of preventing a fast, instantaneous release of large quantities of active material into the solution.

Further, it is known to apply the decontamination agent in the form of a spray, fog or a foam which results in smaller amounts of waste at the cost of more concentrated solutions or long treatment times.

One object of the invented process for decontamination is to offer a process with small amounts of waste, without handling of concentrated treatment agents and with shorter treatment times.

SUMMARY OF THE INVENTION

In order completely or partially to remove a surface layer generated or deposited on the surface, a decontamination agent in the form of a fluid, such as a gas or a gas mixture, a liquid or a liquid mixture, a foam or a gel, is brought into contact with the surface layer, whereby the surface layer is completely or partially disintegrated and/or dissolved. The decontamination agent and the released deposited or generated surface layer are removed and taken care of.

To increase the effect of the decontamination agent, when decontaminating the above-mentioned surface, with a retained low addition of decontamination agent and a short treatment time, microwave fields, that is, an electromagnetic field

with a wavelength within the interval 30 to 0.03 cm and consequently a frequency of between 10^8 and 10^{12} Hz, are applied, according to the invented method, to act on the surface layer and the decontamination agent applied to the surface layer.

Tests have shown that the effect of the applied microwave field is not limited to the heating of the decontamination agent and the surface layer which is obtained but exhibits unexpected improvements of the decontamination effect, which is caused by the effect of the microwaves on reactions between the surface layer and the chemicals in the decontamination agent and thereby on the disintegration of the deposited layer and the penetration of the deposited layer by the decontamination agent and the continued disintegration and to a certain extent the dissolution of the deposited surface layer as well as the removal thereof. Besides, disintegration can be enhanced by uneven microwave energy absorption and volume expansion of the deposited layer. During decontamination with weak solutions, the disintegration of the surface layer is the primary factor whereas the dissolution is often limited.

In a decontamination process where a solution containing a decontamination agent is used, a surfactant or a mixture of surfactants is added and by mechanical means or gas bubbling the agent is transferred into a foam, whereupon this foam is applied to a surface layer to disintegrate, dissolve and remove the surface layer. To improve the decontamination effect while at the same time keeping both the treatment time and the amount of waste low, a microwave field is applied to act on the foam according to the invented method.

According to one embodiment intended to dissolve and remove oxide films containing radioactive nuclides deposited and/or generated on metal surfaces, an acidic or basic foam is

applied to the oxide film, whereupon a microwave field is applied to act on the oxide film and the foam applied to the oxide film to improve the decontamination effect and shorten the treatment time. The foam can also comprise a degreasing agent to dissolve fat layers or agglomerates kept together by the fat, as well as other agents intended to act on other constituents which, like fat, are difficult to penetrate or dissolve using ordinary acidic and/or basic decontamination agents.

An acidic foam preferably comprises a decontamination agent in the form of at least one acid such as, for example, but not limited to, citric acid and oxalic acid, whereas basic foams comprise a decontamination agent such as, but not limited to, a carbonate such as sodium carbonate or a hydroxide such as sodium hydroxide, a water-soluble or colloidal silicate, such as sodium metasilicate.

For formation of foam, at least one surfactant, or a mixture of surfactants, in a content of between 0.1 and 10 per cent by weight is added to the decontamination agent. In one embodiment of the invention, a nonionic surfactant of the type ethoxylated alcohol in a content of between 0.5 and 2 per cent by weight is added to the decontamination agent.

In a preferred embodiment of the invention, a mixture comprising at least one nonionic surfactant of the type ethoxylated alcol combined with an anionic surfactant such as sodium dodecylsulphate in a content of between 0.5 and 2 per cent by weight is added to the decontamination agent. The ratio of nonionic surfactant to anionic surfactant in the surfactant mixture usually amounts to between 1 and 15, preferably to between 5 and 10.

For decontamination of objects that are to be decommissioned, agents that are not suitable for objects to be reused can be

applied, for example hydrofluoric acid, preferably in a concentration of 0.01% to 1%.

Pipe decontamination

For internal decontamination of pipelines, the pipes are filled with a liquid or a foam consisting of one or more organic acids such as oxalic acid or citric acid. The strength of the decontamination agent amounts to between 5 and 50 g/l depending on the desired degree of decontamination. The decontamination agent can also comprise chelating and sequestering agents such as EDTA and NTA in contents of 0.1 to 5 g/l as well as surfactants such as nonionic surfactants of the type primary ethoxylated alcohol combined with an anionic surfactant such as sodium dodecyl sulphate. The total surfactant content amounts to 1 per cent by weight but can be varied within the interval 1 to 10 per cent by weight.

A device for generating and applying a microwave field is led into the pipe via a coaxially arranged conductor. A microwave field with a frequency amounting to between 900 and 10,000 MHz and with a power of 1-2 KW is applied to act on the surface layer and the decontamination agent deposited on the surface layer. The microwaves are applied to act on a section of the surface layer and the decontamination agent deposited on the pipe wall, and by moving the microwave generator-/applicator with cables continuously or by stages through the pipe, the pipe wall is decontaminated continuously or discontinuously. The treatment carried out by chemical means and microwaves may be combined with a mild mechanical treatment such as brushing, water flushing, vibrations or ultrasonics to remove the residues of the surface layer deposited on the pipe wall. After completed treatment, the pipes are rinsed. A layer which inhibits continued deposition may possibly be added or generated. The removed decontamination liquid containing the decontamination agent and released parts of the

surface layer are taken care of, cleaned and deposited by means of ordinary methods. This method is also applicable to internal decontamination of vessels.

Decontamination of components and tools

Components such as valves, pumps, pump parts, etc., included in a plant as well as instruments, gripping devices and tools used for maintenance and operation of the plant must be decontaminated before service and repair and in connection with scrapping.

A decontamination agent to remove oxide layers, fat and/or dirt is applied to act on the surface layer to dissolve, disintegrate and remove the undesired surface layer.

This can be achieved with a plurality of process solutions, such as:

A. Stationary object and stationary decontamination agent. The object to be decontaminated is placed in a vessel of a material transparent to microwaves and resistant to the decontamination agent, for example teflon filled with a liquid decontamination agent with a composition selected based on the composition and property of the surface layer. Alternatively, the object is covered by a foam or a gel comprising a suitable decontamination agent. Thereafter, the vessel is inserted into a microwave oven in which a microwave field is applied to act on the surface layer and the decontamination agent to increase the power and accelerate the degradation and removal of the surface layer. As in pipe decontamination, this treatment can be combined with a mild mechanical treatment before the object is rinsed and possibly after-treated to counteract deposition.

B. Stationary object and circulating decontamination agent.

The object is placed on a surface in a microwave oven and is adapted to be flushed with a decontamination agent in the form of a liquid, a foam or a gel while at the same time applying a microwave field to act on the undesired surface layer and the decontamination agent. The flushed decontamination agent can be recirculated to reduce the consumption and the amount of waste. Different decontamination agents can be applied alternately with or without intermediate rinsings. As described above, the treatment can be supplemented by mechanical methods before the object is washed clean and possibly after-treated.

C. Continuous decontamination.

The objects to be contaminated are placed on a conveyor belt made of a material which is transparent to microwaves and resistant to the decontamination agent. The decontamination agent is applied to the object and a microwave field is applied to act on the surface layer and the decontamination agent while the object is continuously or discontinuously moved on the conveyor belt. The decontamination agent can be applied by flushing one or more decontamination agents in the form of liquids and/or foam over the object. When more than one decontamination agent is used, these agents can be applied simultaneously or alternately. Possibly, the object can be washed clean or treated by mechanical methods between the application of different decontamination agents. Alternately mechanical and chemical/microwave treatment according to the invention can be advantageously carried out even when only one decontamination agent is used.

To apply the microwave field, a plurality of microwave generators/applicators are arranged along the belt to apply a continuous field during the whole treatment, or, according to one embodiment, to apply microwave fields section-by-section. The section-by-section alternative makes it possible to apply the microwaves station-by-station.

The process is well suited to combine the invented chemical/microwave treatment with mechanical methods and to include rinsing and any after-treatment.

Decontamination of large surfaces such as pool walls, vessel walls, etc.

The invented method is also well suited for decontamination of large surfaces such as pool walls, vessel walls, etc., in which case a cover-like member is used, wherein, under the cover, there is arranged at least:

I. Means for supplying a decontamination agent in the form of a liquid, a foam or a gel, and application of the decontamination agent to an undesired surface layer located on the surface;

II. Means for generating a microwave field and application of the microwave field to the undesired surface layer and the decontamination agent, for example one or more spray nozzles;

III. Means for removing surface layer and decontamination agent released from the surface by means of the treatment, for example one or more suction nozzles;

IV. Means for moving the cover above the surface; and

V. Means for achieving a tight contact of the cover against the surface.

The cover can suitably be supplemented by

- means for mechanical removal of the undesired surface layer

- means for application and removal of rinsing fluid (suitably, the same spray and suction nozzles as for application of the decontamination agent can be used), and

- means for application of inhibitors to prevent deposition or some other form of after-treatment.

During treatment, the cover is applied to a part of the surface with an undesired surface layer, which is to be treated, whereupon the treatment is carried out in a conventional way, namely:

- applying the decontamination agent to the surface,

- applying the microwave field to act on the undesired surface layer and the decontamination agent, and

- washing the surface clean.

During the treatment, the decontamination agent can be recirculated to minimize the consumption of chemicals/amount of waste. Removed parts of the surface layer and the decontamination agent as well as rinsing fluid are removed by suction nozzles and are taken care of by conventional methods. After completed treatment, the cover is moved to the next surface region until the entire wall has been decontaminated.

CLAIMS

1. A method for decontamination in which a surface layer generated or deposited on a surface is completely or partially removed, wherein a decontamination agent in the form of a fluid such as a gas, a gas mixture, a liquid, a liquid mixture, a foam or a gel is applied to said surface layer to disintegrate, at least partially dissolve and remove said surface layer, **characterized** in that a microwave field is applied to act on said deposited surface layer and the decontamination agent applied thereto, whereby the penetration of the decontamination agent, the disintegration, dissolution and removal of the surface layer are improved, the treatment time is shortened and the addition of decontamination agent can be kept low.

2. A method according to claim 1, **characterized** in that a decontamination agent in the form of an acid, such as, but not limited to, phosphoric acid, citric acid or oxalic acid, is applied to an undesired surface layer such as an oxide film deposited or generated on a metal surface, and that a microwave field is applied to act on said surface layer and the decontamination agent applied thereto.

3. A method according to claim 1, **characterized** in that a decontamination agent in the form of a basic agent, such as, but not limited to, a carbonate, a hydroxide or a silicate, is applied to an undesired oxide film, and that a microwave field is applied to act on said surface layer and the decontamination agent applied thereto.

4. A method according to claim 1, **characterized** in that a decontamination agent in the form of a degreasing agent is applied to an undesired surface layer containing fat, and that a microwave field is applied to act on said surface layer and the decontamination agent applied thereto.

5. A method according to any of the preceding claims, **characterized** by a solution of at least two cooperating decontamination agents such as, but not limited to, a weak and a strong acid, a weak and a strong base, a degreasing agent and an acid or a base, a chelating or sequestering agent and an acid and a base,
that said decontamination agents are applied to an undesired surface layer, and
that a microwave field is applied to act on said surface layer and the decontamination agent applied thereto.

6. A method according to any of the preceding claims, **characterized** in that a solution comprising at least one foam-forming and foam-stabilizing agent in the form of a surfactant or mixtures of surfactants in a content of 0.1 to 10 per cent by weight is added to the decontamination agent and is transferred into a foam,
that said foam is applied to an undesired surface layer, and
that a microwave field is applied to act on said surface layer and the foam applied thereto.

7. A method according to claim 6, **characterized** in that a solution comprising at least one nonionic surfactant in a content of 0.5 to 2 per cent by weight is added to the decontamination agent.

8. A method according to claim 6, **characterized** in that a solution comprising a mixture of a nonionic surfactant in combination with an anionic surfactant in a total surfactant content of 0.5 to 2 per cent by weight is added to the decontamination agent.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 94/00637

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C23G 1/00, C23G 5/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C23G, B08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI CLAIMS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4816113 (SHUNPEI YAMAZAKI), 28 March 1989 (28.03.89), column 1, line 29 - line 55	1,2,5
P,X	US, A, 5261965 (MEHRDAD M. MOSLEHI), 16 November 1993 (16.11.93), claims 1-2	1
A	US, A, 3712833 (H. FICHAUX), 23 January 1973 (23.01.73), column 4, line 5 - line 45	1-8

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 Sept 1994	11 -10- 1994
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Kerstin Boije Janson Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 94/00637

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

(See extra sheet)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Claim 1 is directed to a method according to which a fluid in combination with microwaves is used to decontaminate a surface. Novelty is lacking for this claim. Lack of unity of invention for the rest of the claims will therefore, a posteriori, arise;

Claims 2 and 5-8 are directed to a method according to which an acid in combination with microwaves is used to decontaminate a surface.

Claims 3 and 5-8 are directed to a method according to which a base in combination with microwaves is used to decontaminate a surface.

Claims 4-8 are directed to a method according to which a degreasing agent in combination with microwaves is used to decontaminate a surface.

INTERNATIONAL SEARCH REPORT

Information on patent family members

30/07/94

International application No.
PCT/SE 94/00637

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4816113	28/03/89	DE-A- 3867867	05/03/92
		EP-A,B- 0280539	31/08/88
US-A- 5261965	16/11/93	NONE	
US-A- 3712833	23/01/73	BE-A- 769686	10/01/72
		CH-A- 531910	31/12/72
		DE-A,B- 2133173	13/01/72
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		GB-A- 1306337	07/02/73
		JP-A- 49005831	19/01/74
		SE-B- 369206	12/08/74